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(54)【発明の名称】 インクジェット紙用被覆組成物およびその製品

## (57)【要約】

つや消し等級被覆インクジェット紙は、全細孔容積0.60乃至2.00 cm<sup>3</sup>/g約90重量%が2ミクロン未満のE. S. D. を有する狭い粒度分布、平均細孔寸法直径0.8ミクロン未満を有する多孔質凝集体からなるか焼カオリン粘土粒状顔料、および1,000乃至5,000、000ダルトンの平均分子量を有するカチオン重合体からなる、被覆組成物で被覆されたセルロース基体からなる。当該重合体は前駆物質スラリー中で分散剤として働き、か焼粘土顔料上に正味の正電荷を与える。この化学処理した粘土顔料を、基体用の最終被覆処方物に使用し、大部分のインクジェット紙に、高い印刷インキ濃度、印刷したおよび被覆光沢、耐水性、低いウィッキング、低いにじみを与える。か焼カオリン粘土は、スラリーの重量基準で約30乃至70重量%固体の高い被覆固体、良好な粘度およびレオロジーを与え、従って、大部分の市販高速コータに適した顔料である。

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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(54) Title: COATING COMPOSITION FOR INK JET PAPER AND A PRODUCT THEREOF			
(57) Abstract			
<p>Matte grade coated ink jet paper comprises a cellulosic substrate coated with a coating composition comprising a calcined kaolin clay particulate pigment comprising porous aggregates with a total pore volume of 0.60 cm<sup>3</sup>/g to 2.00 cm<sup>3</sup>/g, a narrow particle size distribution where about 90 weight % has an E.S.D. less than 2 microns, a mean pore size less than 0.8 microns in diameter, and a cationic polymer with an average molecular weight in the range of 1,000 to 5 million daltons which polymer acts as a dispersant in a precursor slurry and produces a net positive charge on the calcined clay pigment. This chemically treated clay pigment is used in a final coating formulation for the substrate to provide high printing ink density, printed and coating gloss, water fastness resistance, low wicking, and low bleeding on most ink jet papers. The calcined kaolin clay provides a high coating solids of about 30 to about 70 weight % solids, based on the weight of the slurry, and good viscosities and rheology, therefore, making the pigment suitable for most commercial high speed coaters.</p>			

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TITLE OF THE INVENTION

COATING COMPOSITION FOR INK JET PAPER AND A PRODUCT THEREOF

BACKGROUND OF THE INVENTION5 1. Field Of The Invention

This invention relates generally to ink jet paper used in ink jet printing and, more particularly, to a coating composition suitable for making matte grade coated ink jet paper. The improvement relates to the use of a paper coating composition primarily of an engineered kaolin clay which is treated  
10 with a cationic polymer.

2. Description Of Related Art

In ink jet printing, uniformly shaped droplets of aqueous or solvent-based dye solutions are ejected from a nozzle onto a paper or other substrate. The paper and surface chemistry requirements for good print  
15 quality vary widely and may rely on coating materials to create appropriate ink sorption characteristics.

Ink jet inks may be water-based or may have an alkylene glycol or other solvent base.

For the printing of well shaped dots by means of ink jets, and  
20 especially for multi-color printing with ink jets, the use of paper coated with a pigment is highly desirable. The pigment and the binder of the coating may generally serve to sorb the solvent of the ink (i.e. dry the ink) and hold the dye stuff of the ink on the surface of the coating to maximize the visual effect of the ink.

25 A binder used in a paper coating generally serves the function of holding the pigment so as to reduce or eliminate dusting or chalking thereof, since ink jet printers with very fine orifice nozzles are quite susceptible to clogging. Also, the binder should help in the sorption of the solvent of the ink. If too high a binder is used, ink will remain on the surface and will smear  
30 or even splatter when hitting the surface after ejection from the nozzle. Too weak a binder will not hold the pigment without chalking.

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U.S. Patent No. 4,892,787 issuing on January 9, 1990 discloses a cellulosic substrate coated with a mixture of a particular pigment having a surface range of about 100 to 350 m<sup>2</sup>/g and an average particle size of less than about 8 μm, and a binder comprising a mixture of an acrylic resin and  
5 polyvinyl alcohol in effective amounts to minimize chalking of the pigment and to sorb solvent from the water-or glycol-based jet printing ink. The pigment is selected from the group consisting of silica, alumina, silica-aluminum and titania.

The teachings of this U.S. Patent No. 4,892,787 provide a coating  
10 with fractal dimension of less than 1.1 and aspect ratios of less than 1.1, as exhibited by dots formed by ink jet printers on the coating disclosed therein. The coating does not chalk, but other printing performance factors of the ink jet paper, such as color ink densities, ink drying rate, water fastness resistance, wicking and bleeding are not addressed in this U.S. Patent No.  
15 4,892,787.

U.S. Patent No. 5,281,467 issuing on January 25, 1994 discloses an ink jet recording paper with a coating containing a pigment which achieves excellent ink absorption, smoothness, gloss, and water resistance together with an excellent dot density, sharpness, and roundness to ensure recording  
20 of high quality, high contrast full color images. The coating is applied to a support by a cast coating method, and the pigment comprises at least 50 weight percent of a calcium carbonate-compounded silica. The average particle size of the compound silica is no greater than 3 μm in order to increase dot sharpness and density. The specific surface area of the  
25 compound silica as measured by the BET method is preferably no greater than 80 m<sup>2</sup>/g. A binder is added to the coating composition in order to improve adhesion of the pigment to the support and render the coating uniform. It is also desirable that the coating contain a cationic polymer to improve the water resistance of the recorded image. Some disadvantages of  
30 the coating of this U.S. Patent No. 5,281,467 is that the coating composition

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in slurry form contains low coating solids, poor rheology, and is expensive to manufacture.

U.S. Patent No. 4,554,181 issuing on November 19, 1985 to the Mead Corporation discloses an ink jet recording sheet having a recording surface  
5 which includes a combination of a water soluble polyvalent metal salt and a cationic polymer having cationic groups which are available in the recording surface for insolubilizing an anionic dye. The recording surface may be formed by applying an aqueous solution of the aforesaid salt and polymer to the surface of an absorbent sheet material such as paper or by applying a  
10 coating containing the polymer and salt combination alone or in combination with a binder which may be water swellable, and other additives, to the surface of a substrate, such as paper or plastic film. The combination of the salt and cationic polymer achieve images of improved density, water fastness, and sharpness. Coated paper products can be prepared by  
15 incorporating a water soluble polyvalent metal salt and a cationic polymer or latex into a conventional paper coating composition and applying the coating to the paper substrate using conventional coating techniques. Such conventional coatings typically include a white pigment such as clay, diatomaceous earth, baryta, and/or calcium carbonate, and a binder such as  
20 gelatin, etherified starch, or polyvinyl alcohol.

U.S. Patent No. 4,425,405 to Mjrakami et al. describes a coating composition containing a white filler and polyvinyl pyrrolidone. Preferably, the salt and the cationic polymer are added to this coating composition in an amount of about 0.1 to 30 parts per 100 parts composition.

25 U.S. Patent No. 5,270,103 to Oliver et al. discloses the use of coated ink jet sheets comprising a silicate or silicate pigment with a two component binder of polyvinyl alcohol and cationic polymers, including polyamines, to improve color density.

The prior art, including that described hereinabove, disclose specific  
30 means and/or methods for achieving certain objectives, such as high image

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quality, such as high color sharpness and high resolution or high printing performance, such as reduced offset, feathering, paper curl, and improved water fastness, and the prior art has several drawbacks and disadvantages. In some of the teachings of the prior art, the density, sharpness, and  
5 roundness of each dot still may not be good enough to obtain high quality, high contrast, full color recorded images for ink jet paper.

Some coating compositions, such as silica-based coatings, applied to a substrate, tend to produce an ink jet paper with a relatively high print performance. However, the costs for these commercially available papers  
10 with silica coatings tend to be high due to the raw materials and the manufacturing process.

It would be ideal to have commercially available, an ink jet paper with at least the same or better quality print performance as those with the silica-based coating compositions, but produced at a lower manufacturing cost  
15 and at higher coat weights to increase opacity for two-sided printing.

#### SUMMARY OF THE INVENTION

It has been found that surprising results were obtained by preparing an ink jet coating slurry comprising calcined kaolin clay pigment which is porous and has a narrow particle size distribution and an effective amount of cationic  
20 polymer. The treated pigment, in dry form or in slurry form, may be prepared for shipping purposes as a precursor coating for ultimate use in a final coating formulation applied to paper to produce a matte grade coating ink jet paper. The specially designed pigment, the cationic polymer/pigment/binders ratio, and the molecular weight of the cationic polymer contribute to improve dot  
25 density and dot roundness, and water fastness resistance and reduced feathering and offset for a matte grade coated ink jet paper. The particle size distribution of the calcined kaolin clay pigment is such that about 90 weight % is less than 2 microns in equivalent spherical diameter.

The cationic polymer of the invention possesses a net positive charge  
30 and is preferably a polymeric amine such as a polymer of quaternary amines

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or amines which are converted to quaternary amines under acid conditions. The cationic polymer may also contain two or more cationic monomers or contain a cationic monomer and other non-ionic or anionic monomers. These cationic polymers possess a molecular weight from about 1,000 daltons to about 5,000,000 daltons, as determined by gel permeation chromatography. Physical blends of cationic polymers containing different cationic moieties or blends of cationic polymers possessing different molecular weight averages and distributions are also contemplated within the scope of this invention.

It is therefore an object of the invention to provide an ink jet recording surface with a final coating composition having good ink drying, and ink absorption, and/or water resistance with low wicking and bleeding together with an acceptable dot density, sharpness and roundness, and which is suitable for the recording of high quality, high contrast full color images.

It is a further object of the present invention to provide an ink jet recording surface with a final coating composition which results in print performance which is at least equal to or better than silica coatings but less expensive than the raw materials and manufacturing costs of silica coatings, and in higher coating solids which may result in higher coat weights and better coating rheology in comparison to the silica coatings, and which coating composition can be used in a whole variety of conventional coaters.

The aforesaid objects of the invention are attained by an ink jet recording paper having a support provided on at least one surface with a final coating composition where a precursor coating composition comprises kaolin clay pigment chemically treated with a cationic polymer and which precursor coating composition is characterized in that the aqueous slurry contains about 30 to 70 weight % solids, based on the weight of the slurry, and the ratio of the pigment to the polymer in this slurry ranges from about 10 to about 1.

In accordance with an embodiment of the present invention, an improved ink jet paper has a precursor coating composition comprising a porous calcined kaolin clay pigment and a medium to high molecular weight

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cationic polymer. The molecular weight of the cationic polymer is about 1,000 to 5 million daltons. The total pore volume of the pigment is about 1.00 cm<sup>3</sup>/g to about 1.50 cm<sup>3</sup>/g by mercury porosimetry. The mean pore size is between 0.1 to 0.8 microns and perhaps between 0.1 to 0.5 microns in diameter. The particle size distribution is such that about 100% by weight are less than 10 microns E.S.D.; about 98% by weight are less than 5 microns E.S.D.; about 90% by weight are less than 2 microns E.S.D.; about 80% by weight are less than 1 micron; about 30% by weight are less than 0.5 micron E.S.D.; and about 2% by weight are less than 0.25 micron E.S.D.

10 The cationic polymer acts primarily as a dispersant in the slurry form resulting in a high percent solids by weight of about 30 to 70 weight % solids. This precursor coating composition is then employed in a final coating composition where the coating formulation comprises 100 parts of the precursor coating composition, and to this is added about 20 to 30 parts polyvinyl alcohol used

15 as a binder; 30 to 50 parts latex used as a binder; 1 to 5 parts cross-linking agent used to cross-link the binders; and 0 to 3.0 parts optical brightening agent added to form a final coating composition of about 30 to 70 weight % solids, based on the weight of the slurry. The ratio of chemically treated pigment with cationic polymer to polyvinyl alcohol binder to latex binder on a

20 dry basis ranges from about 1:0.15:0.05 to about 1:1:1.6 which is used in a final coating composition.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a coating composition which comprises: a) an aqueous slurry containing about 30 to about 70 weight

25 % solids, based on the weight of said aqueous slurry, of a calcined kaolin clay, preferably about 30-40%, more preferably about 32 to about 35%; and

b) an effective amount of a cationic polymer or cationic polymer admixture, wherein said cationic polymer or cationic polymer admixture reacts with said calcined kaolin clay and wherein said effective amount is an amount of

30 cationic polymer sufficient to produce a net positive charge on said calcined



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kaolin clay. Generally, about 5 to about 50 parts (on an active weight basis) of cationic polymer should be used per 100 parts of calcined kaolin clay.

Preferably, the ratio is about 10 to about 40 parts per 100 parts clay, more preferably about 20 to about 30 parts per 100 parts clay. Preferred cationic

- 5 polymers are selected from the groups consisting of polyamines, polydialkyldiallylammonium halides and polymers prepared by polymerizing a dialkyldiallylammonium halide with another ethylenically unsaturated cationic, anionic or nonionic monomer. The preferred dialkyldiallylammonium halide monomers are dimethyl or diethyl dialtylammonium chloride, with
- 10 dimethyldiallylammonium chloride polymers being most preferred in this class.

Admixtures containing a cationic polymer and one or more additional polymers can also be used. The key is to provide sufficient cationic polymer (either as a single cationic polymer or multiple cationic polymers) to provide a net positive charge on the calcined kaolin clay being treated.

- 15 The molecular weight of the instant cationic polymers ranges between about 1000 and about 5 million daltons, preferably between about 250,000 and about 1 million daltons. The preferred calcined kaolin clay in aggregate form has a mean pore size less than about 0.80 microns in diameter, and a particle size distribution wherein about 90% are less than 2 microns E.S.D.
- 20 Further, the preferred calcined kaolin clay has a total pore volume of about 0.60 cm<sup>3</sup>/g to about 2.00 cm<sup>3</sup>/g. More preferably, the calcined kaolin clay, in aggregate form, has a particle size distribution wherein about 100 weight % are less than 10 microns E.S.D.; about 98 weight % are less than about 5 microns E.S.D.; about 90 weight % are less than about 2 microns E.S.D.;
- 25 about 80% are less than about 1 micron E.S.D.; about 30 weight % are less than about 0.5 micron E.S.D.; and about 2 weight % are less than 0.25 micron E.S.D.

- The instant coating compositions may additionally comprise about 20 to about 30 parts by weight (on an active basis) per 100 parts by weight
- 30 calcined kaolin clay, of a polyvinyl alcohol binder; about 30 to about 50 parts

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by weight (on an active basis) per 100 parts by weight calcined kaolin clay, of a latex binder; and about 0 to about 5.0 parts by weight (on an active basis) per 100 parts by weight calcined kaolin clay, of a cross-linking agent, wherein the crosslinking agent, if used, acts to crosslink said binders.

- 5 Preferably, the ratio of calcined kaolin clay to polyvinyl alcohol binder to latex binder on a dry, active weight basis ranges from about 1.0:0.15:0.05 to about 1:1:1.6.

The coating compositions are applied to coating substrates, preferably paper substrates. More preferably, the substrate is a substrate useful in ink  
10 jet printing.

The instant invention is also directed to compositions comprising: a) a coating substrate; and b) an effective amount of the above described coating compositions, wherein effective amount refers to the quantity of coating composition necessary to effectively coat the substrate being treated.

- 15 Preferably, the substrate is a paper substrate and more preferably the substrate is a substrate useful in ink jet printing.

The instant invention is further directed to a method of preparing a coating composition for coating a substrate, comprising: a) preparing a calcined kaolin clay aqueous slurry containing about 30 to about 70 weight  
20 % solids, based on the total weight of said aqueous slurry; and b) adding an effective amount of at least one cationic polymer to the aqueous slurry, thereby dispersing the calcined kaolin clay and producing a net positive charge on the calcined kaolin clay. This method may further comprise the steps of adding about 20 to about 30 parts by weight (on an active basis) per  
25 100 parts by weight of calcined kaolin clay, of a polyvinyl alcohol binder; about 30 to about 50 parts by weight (on an active basis) per 100 parts by weight of calcined kaolin clay, of a latex binder; and about 0 to about 5.0 parts by weight (on an active basis) per 100 parts by weight of calcined kaolin clay, of a cross-linking agent.

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Preferably the ratio of clay to polyvinyl alcohol binder to latex binder on a dry active basis ranges from about 1.0:0.15:0.05 to about 1.0:1.0:1.6.

This method may additionally comprise drying the resulting product to produce a substantially moisture-free calcined clay pigment coated with the cationic polymer employed. The dried product may then be filtered, preferably through at least a 50 mesh sieve and then optionally through a 100 mesh sieve, to remove undispersed particles and agglomerates.

Thus, the coating composition of the instant invention for ultimate use as a coating on at least one side of a web comprises an aqueous slurry of the components described herein.

A suitable calcined kaolin clay pigment for use in the invention substantially corresponds to the commercially available product ALPHATEX<sup>®</sup> of the present assignee, ECC International Inc. (Atlanta, Georgia). The manner in producing this ALPHATEX<sup>®</sup> product is taught in McConnell et al., U.S. Patent No. 4,381,948, which is incorporated herein by reference. This ALPHATEX<sup>®</sup> product is prepared by first blunging and dispersing an appropriate crude kaolin to form an aqueous dispersion of same. The blunged and dispersed aqueous slurry is subjected to a particle size separation from which there is recovered a slurry of the clay, which includes a very fine particle size, e.g., substantially all particles are smaller than 1 micrometer E.S.D. The slurry is dried to produce a relatively moisture-free clay, which is then thoroughly pulverized to break up agglomerates. This material is then used as a feed to a calciner. Such feed is calcined under carefully controlled conditions to typical temperatures of at least 900°C. The resulting product is cooled and pulverized to provide a pigment of porous aggregates of kaolin platelets. For the invention, this final pulverization step for the calcined

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product produces the desired clay particle size distribution as set forth below, (E.S.D. refers to equivalent spherical diameter):

- 100 weight % has an E.S.D. of < 10 microns
- about 98 weight % has an E.S.D. of < 5 microns
- 5 about 90 weight % has an E.S.D. of < 2 microns
- about 80 weight % has an E.S.D. of < 1 micron
- about 30 weight % has an E.S.D. of < 0.5 micron
- about 2 weight % has an E.S.D. of < 0.25 micron

This final pulverization step involves a dry grinding process in a conventional  
10 ball mill. This ALPHATEX<sup>®</sup> product has generally been used as a filler in paper sheets and similar paper products in view of its porous aggregates and its high light-scattering ability. The present invention finds this product to be exceptionally suitable as a coating pigment for making matte grade coated ink jet paper. Its porous aggregates of kaolin clay platelets act to create a  
15 coating porosity for good ink absorption.

The porous aggregates which compose the particles, are believed to be instrumental in producing outlets for the aqueous ink to penetrate vertically through the coating layer without ink spreading or wicking, by virtue of their high porosity, which porosity, in turn, is defined by the total pore volume and  
20 the mean pore size. The mean internal pore size of the aggregate is generally less than 0.80 microns in diameter. The total pore volume of the porous aggregates is about 0.60 cm<sup>3</sup>/g to about 2.00 cm<sup>3</sup>/g. Large pore diameters provide a porosity which is thought to allow the ink vehicle to penetrate to the coating for complete ink drying.

25 Certain cationic polymers may be used as retention aids in the paper industry. Cationic polymers can be used in the recording surface for dye insolubilization when they are added to the paper after sheet formation. When used as retention aids, these polymers are added at the wet end of the paper making process where they pick up counter ions which will not  
30 exchange for the anionic dye. In conventional papers in which these

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polymers are used as retention aids, the polymers do not contain cationic groups which are available for dye insolubilization.

In the present invention, an excess of cationic polymer is used to neutralize, through salt formation, a sufficient number of negatively charged sites on the surface and edges of the calcined clay particles to create particles possessing a net positive charge to react with an anionic dye or ink. As used herein, the term "effective amount of cationic polymer" is that amount of cationic polymer which at least creates clay particles possessing this net positive charge.

10 In accordance with a preferred embodiment of the invention, the cationic polymer is water soluble and is used generally as a dispersant in the aqueous slurry containing the calcined kaolin clay pigment.

A representative example of a commercially available polymer that is useful in the invention is Hydraid 2060, a polyamine product available from Calgon Corporation, Pittsburgh, PA. This polymer is about 50% active and has a molecular weight greater than 100,000 daltons.

The suitable polymer for use in this invention, i.e., Hydraid 2060, is a branched polymer derived from the condensation reaction of dimethylamine, epichlorohydrin, and small amounts of a primary amine, such as methyl amine, or ammonia. As a quaternary ammonium polymer, 100 mol % of the monomer units are cationic.

The surface of a calcined clay usually carries a net negative charge. It is theorized by the inventors that mixing of the cationic polymer with the anionic clay results in the reaction of the polymer at the negatively charged sites on the surface of the clay to form a salt bond between the clay surface and the polymer. A single polymer strand may react with multiple sites on the surface of a single clay particle or bridge sites between particles, causing particle aggregation or coagulation. In the presence of sufficient cationic polymer, many of the negative sites on the surface of the calcined clay are neutralized and the clay surface acquires a net positive charge. The presence

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of this net positive charge provides the energy needed to repulse or disperse other clay particles, thus the cationic polymer of the invention acting as a dispersant in the aqueous slurry containing the calcined kaolin clay particles.

Since cationic polymers are generally hygroscopic, i.e., water-  
5 absorbing, there is a critical range of cationic polymer to clay ratio needed to bond with and to cationize the surface. Below this dosage range the surface still has a net negative charge. Above this dosage range, the surface is cationic, but coated with excess polymer and too hygroscopic. The amount of polymer needed to cationize the clay surface and the chemical nature of  
10 the coating will vary with polymer molecular weight, composition, and three dimensional structure.

Most ink jet inks are anionic or amphoteric (having negative and positive charge groups in the same molecule). When the ink is deposited onto the surface of the polymer treated clay, salt bonds are formed between  
15 the cationic polymer and the anionic groups, usually sulfonic acids, on the ink/dye molecule. This reaction fixes the ink to the surface. Additional weak bonds, e.g., hydrogen bonding and Van der Waals bonds, are formed between the polymer, clay and dye molecules to provide multiple points of attachment for the ink/dye. It is believed that as the number of bonds  
20 between the ink and polymer/clay surface increase, the energy needed for a solvent like water to break all of these bonds at once to free the ink increases significantly. Consequently, the printed surface becomes water fast.

Preferably, the cationic polymer of the invention is a polymeric amine, such as a polymer of quaternary amine or amines which are converted to  
25 quaternary amines under acid conditions.

Cationic polymers which may be used in the invention may be polyamines, or polymers and copolymers of dialkyldiallylammonium halides or admixtures thereof.

Cationic polymers which may be used in the invention are generally  
30 characterized as having an active basis from about 8% to about 50% and a

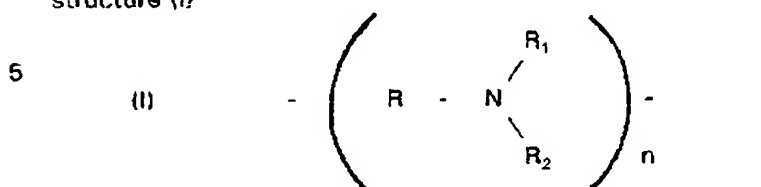
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molecular weight from about 1,000 daltons to about 5 million daltons.

Representative polymers are linear or branched polyamines represented by structure (I)



10 wherein  $R_1$  and  $R_2$ , which may be the same or different, are selected from the group consisting of straight or branched  $C_1$ - $C_8$  alkyl, substituted straight or branched  $C_1$ - $C_8$  alkyl and hydrogen; wherein  $R$  is selected from the group consisting of straight or branched  $C_1$ - $C_8$  alkyl and substituted straight or branched  $C_1$ - $C_8$  alkyl, and wherein  $n$  ranges from 2-50,000.

15 Other cationic polymers are linear or branched polymers of cationic monomers, such as alkyl- or dialkyldiallylammonium halides, especially dimethyldiallylammonium chloride, dimethylaminoethylmethacrylate and its methyl chloride or dimethyl sulfate quaternary ammonium salts, dimethylaminoethylacrylate and its methyl chloride salt,  
20 methacrylamidopropyltrimethylammonium chloride and its unquaternized amine form, acrylamidopropyltrimethylammonium chloride and its unquaternized amine form. Other cationic polymers include condensates of formaldehyde with melamine, urea, or cyanoguanidine.

The cationic polymers useful in this invention also include copolymers  
25 of the aforementioned cationic monomers with nonionic monomers, such as acrylamide, methacrylamide, vinyl acetate, vinyl alcohol, N-methylolacrylamide, or diacetone acrylamide, and/or anionic monomers, such as acrylic acid, methacrylic acid, AMPS, or maleic acid, such that the net charge of these polymers is cationic.

30 Examples of other commercially available cationic polymers useful in the invention are Hydraid 2010; Hydraid 2020; Hydraid 2030; Hydraid 2040; Hydraid 2070; Hydraid 2080, which are polydimethyldiallylammonium

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chlorides (p-DMDAAC); and Hydrad 2050, a polyamine, all of which have a molecular weight of from about 2,000 to 5 million daltons, and all of which are products available from Calgon Corporation, Pittsburgh, PA.

One embodiment of the present invention is to provide a coating composition for a base stock to produce a matte grade ink jet paper for use in ink jet printing. Preferably, the substrate is comprised of any of a variety of papers, including wood-based and rag-based papers, such as vellum. However, those skilled in the art will appreciate that the invention may be applied to any of a wide variety of substrates, such as synthetic paper or plastic film, as circumstances dictate.

The coating composition of the invention is formed by mixing an engineered calcined kaolin clay pigment having certain physical characteristics, such as the particle size distribution, the total pore volume, and the mean pore size, disclosed hereinabove, with a cationic polymer which is used to chemically treat this specially designed pigment.

Throughout the description of the invention, where "parts" for the chemicals used in the invention are given, it is to be interpreted as parts by weight per 100 parts by weight of the pigment.

The coating composition comprises an engineered kaolin clay pigment chemically treated with a cationic polymer with a medium to a high molecular weight, from about 1,000 daltons to about 5 million daltons, preferably about 100,000 to 2 million daltons and, most preferably, about 250,000 to about 1 million daltons. This composition is formed by making an aqueous slurry where about 5 to about 50 parts by weight, more preferably about 10 to about 40 parts by weight and, most preferably, about 19 to about 27 parts by weight of cationic polymer per 100 parts of pigment by weight, on a dry basis, is first mixed with a proper amount of warm solvent (water) at a temperature of 30 to 40° Celsius. The calcined kaolin clay is gradually added to and mixed with the chemical/solvent for complete pigment dispersion until a 30 to 40 weight % solids, and preferably about 30 to 70 weight % solids,



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coating slurry is formed. The dispersed slurry is then filtered first through a 50 mesh screen, and then through a 100 mesh screen for removing the undispersed particles and agglomerates. The filtered product is then ready to be shipped to the end user, which may be a paper manufacturer. This

5 coating composition preferably, in slurry form, is a precursor for the final coating applied onto the substrate. If a dry form of the product of the invention is desired, then the slurried product can be dried by conventional means such as a spray dryer to produce a moisture-free calcined clay pigment coated with the cationic polymer.

10 As a final coating composition which is applied to the substrate, this precursor coating composition is preferably mixed with additional chemicals. The following provides a preferred final coating formulation which may be used by a paper manufacturer.

A Preferred Final Coating Formulation

15 To a 100 parts of the precursor coating composition, in slurry form, comprising the calcined clay pigment and the cationic polymer, add the following:

23.4 Parts : Polyvinyl Alcohol (PVOH) (a binder)

36.2 Parts : Latex (a binder)

20 1.7 Parts : Cross-linking Agent

3.0 Parts : Optical Brightening Agent

Suitable polyvinyl alcohols are characterized as being hydrophilic, cross-linkable with the cross-linking agent, and film-forming. A suitable polyvinyl alcohol is available from the Air Products Co. under the tradename

25 AIRVOL<sup>®</sup> 103, which is 98.0 to 98.8% hydrolyzed, has a pH of 5.0 to 7.0., and a molecular weight of 13,000 to 23,000 daltons. Other polyvinyl alcohols which may be suitable in the invention are available from DuPont under the trade designations Elvanol 71-30 and HV. Elvanol 71-30 polyvinyl alcohol is 98% hydrolyzed, has a pH of 6, and has a medium molecular

30 weight as measured by viscosity. DuPont Elvanol HV polyvinyl alcohol is 99-

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TABLE I

5	Coating Formulation:		100 parts
	Pigment		20 parts
	PVOH		50 parts
	Latex		5 parts
	Cross-Linking Agent		
10	Coating Results:		
		Invention	Prior Art
		(Calcined Clay)	(Silica)
	% Coating Solids	38.36	25.19
	pH	7.4	5.8
15	Brookfield Viscosity		
	Spindle #	6	5
	@ 10 rpm	21,800 cps	4,400 cps
	@ 20 rpm	13,250 cps	6,000 cps
	@ 50 rpm	6,720 cps	2,840 cps
20	@ 100 rpm	4,300 cps	1,872 cps
	Harcules Viscosity		
	@ 4400 (kilodynes-cm)	5,500 cps	2,000 cps
25	Coated Sheet Properties @ 8 g/m <sup>2</sup> Coat Weight		
	Brightness (ISO)	88.94	90.62
	OBA *	0	0
	Hunter		
30	L	93.37	94.19
	a	0.75	0.64
	b	-0.93	-1.28
	Opacity	95.06	95.23
35	Sheet Gloss	5.22	2.84
	Printing Properties		
	Ink Density		
40	Cyan	1.46	1.80
	Magenta	1.48	1.50
	Yellow	1.12	1.08
	Black	1.63	1.82
	Bleeding	Minimum	Minimum
45	Wicking	Minimum	Minimum
	Print Gloss		
	Cyan	5.9	2.1
	Magenta	4.7	2.2
	Yellow	4.5	2.7
50	Black	20.2	4.6
	Ink Drying		
	Primary Colors (CMY* *)	Fast	Fast
	Secondary (RGB* **)	Fast	Fast
	Black	Slow	Slow
55	Water Fastness Resistance	Yes	Yes
	* "CMY" Means Cyan, Magenta, and Yellow.		
	** "RGB" Means Red, Green, and Blue.		
	*** "OBA" Means Optical Brightening Agent.		
60	The conclusions made from this study were:		
	1) The percent solids for the coating composition of the invention		
	was 13 percent higher than that of the prior art containing silica.		

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100% hydrolyzed, has a pH of 6 and a high molecular weight as measured by viscosity.

A suitable latex is characterized as being "pigment interactive". Such a suitable latex is available from Dow Chemical U.S.A., Midland, Michigan

5 under the tradename Latex CP 654NA. This latex is a carboxylated styrene-butadiene latex which is designed for use with starch as a cobinder in pigmented paper coatings and where its pigment interaction characteristics contribute to quicker coating set, resulting in improved fiber coverage and coating smoothness.

10 A suitable cross-linking agent is characterized as cross-linking the polyvinyl alcohol binder with the latex binder to improve the water fastness or water resistance of the recorded image. Such a suitable cross-linking agent is water soluble, and has sufficient active sites on their molecules to react with the binders to efficiently cross-link these components. A suitable  
15 cross-linking agent is available from Hopton Technologies, Inc., Albany, Oregon, under the tradename HTI Insolubilizer 5800M Ammonium Zirconium Carbonate (AZC), which is a metallic ion.

Where coating formulation is given herein involving the inventive pigment, the chemicals used were as follows: the polyvinyl alcohol was  
20 Airvol<sup>®</sup> 103, the latex binder was Latex CP 654NA, the cross-linking agent was HTI 5800M Ammonium Zirconium Carbonate (AZC), and the optical brightening agent, if used, were those conventionally available and known to those skilled in the art.

#### Lab Procedure For Forming Precursor Coating Slurry

25 The engineered calcined clay treated with a cationic polymer according to the teachings of the invention was made available for shipping to a paper manufacturer in a 32% weight % solids for making matte finish coated ink jet paper. This aqueous slurry was comprised of the engineered calcined clay and the cationic polymer, as disclosed hereinabove. The calcined clay was  
30 made through the normal process for making the ALPHATEX<sup>®</sup> product as

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disclosed in the aforesaid McConnell et al. U.S. Patent No. 4,381,948, and then pulverized in a ball mill to the desired particle size distribution.

Lab results showed that the clay particle size distribution in equivalent spherical diameter (e.s.d.) of the calcined clay pigment used in the following

5 examples of the invention were:

100 weight % < 10 microns

98 weight % < 5 microns

90 weight % < 2 microns

80 weight % < 1 micron

10 30 weight % < 0.5 microns

2 weight % < 0.25 microns

The aqueous slurry was prepared by measuring out about 20-22 parts by weight per 100 parts by weight of the calcined clay pigment, of the cationic polymer and then transferring this polymer to a simple mixing tank that is

15 equipped with high speed/ low shear mixing blades. A proper amount, of about 70% of total batch weight for the slurry, of warm tap water at about 30 to 40° Celsius was pumped into the mixing tank. Initially, the chemical/water solution was mixed at a blade speed of 1000 rpm (revolutions per minute) for 5 minutes, being careful to avoid the polymer from sticking to

20 the mixing spindle. Since the polymer has a high viscosity of about 2,000 to about 4,000 centipoise (cps), it has a tendency to climb up the mixing spindle. The blade speed was then increased to 2000 rpm and the solution was mixed for another 5 minutes. The dry calcined pigment was added to this solution at a slow feed rate at about 1 to 2 lbs./minute until the pigment

25 was completely dispersed in the chemical/water solution. If necessary, the mixer speed can be increased for this pigment dispersion. For a thorough clay/chemical dispersion in the slurry, the clay/chemical slurry should be mixed at a blade speed between 1000 - 2000 rpm for 15 minutes. The dispersed slurry was then filtered first through a 50 mesh sieve, and then

30 through a 100 mesh sieve where the undispersed particles and agglomerates

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were removed. The filtered product, in slurry form, comprising 32% weight % solids, was then ready for shipment to a potential end user.

#### Final Coating Composition

Preferably, the chemically treated clay pigment is shipped in slurry form and used in a final coating composition where the coating formulation comprises the precursor coating composition. To this, about 20 to 30 parts by weight of polyvinyl alcohol; 30 to 50 parts by weight of latex; 1 to 5 parts by weight of cross-linking agent; and 0 to 3.0 parts by weight of optical brightening agents per 100 parts by weight of pigment are added to form a final coating composition of about 30% to about 70% solids.

#### Lab Scale Samples

The coating composition of the invention comprising the specially engineered kaolin clay pigment is preferred by the inventors in view of the low manufacturing costs due to low energy consumption and capital investment. Lab scale samples were made and tested for its slurry stability in a 30 day period. The Helios low shear viscosity results indicated that the slurry was highly stable with no viscosity change during this 30 day test. The kaolin clay slurry of the invention was able to be made down easily into a coating color that was more stable than the silica coatings of the prior art. Unlike coater limitations of most silica coatings, the inventive coating composition can be applied by various types of coaters, including the metering size press, rod, gate roll, and blade coaters.

#### Application Testing

Application testing was performed in four different ways: 1) lab hand draw down; 2) hand draw down vs. commercial coated ink jet paper; 3) first coating trial; and 4) second pilot coating trial. Where a coating formulation involving the inventive pigment, the chemicals used were as follows: the polyvinyl alcohol was Airvol® 103; the latex binder was Latex CP 654NA; and the cross-linking agent was HTI 5800M Ammonium Zirconium Carbonate (AZC).

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1) Ink Jet Coating Lab Hand Draw Down Study

The objective of this study was to compare the coating composition of the invention comprising the chemically treated calcined clay to that of the prior art containing silica as a pigment with regard to coated sheet properties and printing properties. The same coating formulation was used in both coating compositions, with only the type of pigment differing with that of the invention being the specially designed calcined clay chemically treated with a cationic polymer in accordance with the teachings of the present invention. The coating formulation and results are shown in Table I.

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TABLE I

5	Coating Formulation:		
	Pigment	100 parts	
	PVOH	20 parts	
	Latex	50 parts	
	Cross-Linking Agent	5 parts	
10	Coating Results:		
		Invention	Prior Art
		(Calculated Clay)	(Silica)
	% Coating Solids	38.36	25.19
	pH	7.4	5.8
15	Brookfield Viscosity		5
	Spindle #	8	4,400 cps
	@ 10 rpm	21,800 cps	5,000 cps
	@ 20 rpm	13,250 cps	2,840 cps
	@ 50 rpm	8,720 cps	1,872 cps
20	@ 100 rpm	4,300 cps	
	Hercules Viscosity		
	@ 4400 (kilodynes-cm)	5,500 cps	2,000 cps
25	Coated Sheet Properties @ 8 g/m <sup>2</sup> Coat Weight		
	Brightness (ISO)	88.94	90.62
	OBA*	0	0
	Hunter		
30	L	93.37	94.19
	a	0.75	0.64
	b	-0.93	-1.28
	Opacity	95.08	95.23
	Sheet Gloss	5.22	2.84
35	Printing Properties		
	Ink Density		
40	Cyan	1.40	1.60
	Magenta	1.48	1.50
	Yellow	1.12	1.08
	Black	1.83	1.82
	Bleeding	Minimum	Minimum
	Wicking	Minimum	Minimum
45	Print Gloss		
	Cyan	5.9	2.1
	Magenta	4.7	2.2
	Yellow	4.5	2.7
	Black	20.2	4.6
50	Ink Drying		
	Primary Colors (CMY**)	Fast	Fast
	Secondary (RGB***)	Fast	Fast
	Black	Slow	Slow
55	Water Fastness Resistance	Yes	Yes

\* "CMY" Means Cyan, Magenta, and Yellow.

\*\* "RGB" Means Red, Green, and Blue.

\*\*\* "OBA" Means Optical Brightening Agent.

60

The conclusions made from this study were:

- 1) The percent solids for the coating composition of the invention was 13 percent higher than that of the prior art containing silica.

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2) Both compositions exhibited similar performance with respect to color ink densities, ink drying rate, water fastness resistance, wicking, and bleeding.

3) The brightness value for the coating composition of the invention was 1.7 points lower than that of the prior art coating composition, indicating the potential need for using an optical brightening agent in the slurry to increase brightness of the composition of the invention. This brightening agent was included in the recommended coating formulation disclosed hereinabove for the present invention. The optical brightening agents are well-known in the art and several are readily available and commonly used.

4) Both sheet gloss and print gloss for the invention were significantly improved over that of the prior art.

2) Hand Draw Down vs. Commercial Coated Ink Jet Paper

The objective of this study was to compare the printing performance of a paper coated with the coating composition of the invention to that of a commercially available paper coated with a silica coating of the prior art. The base stock of the paper coated with the composition of the invention was a non-sized free paper of basis weight 90 g/m<sup>2</sup> Hammermill laser print, and that of the commercially available paper was made by Otis Specialty, Inc., Maine. It is not certain as to the coating formulation of the commercially available paper. The coating formulation of the coating composition of the invention was in accordance with that disclosed hereinabove with regard to Table I for the first lab hand draw down study. The results of this test are shown in Table II.

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TABLE II

Printing Performance:			
		Commercial Paper (Silica)	Invention (Calcined Kaolin Clay)
5	Ink Density		
	Cyan	1.47	1.46
10	Magenta	1.45	1.36
	Yellow	1.12	1.05
	Black	1.27	1.63
	Dot Size (Magenta)		
	Average (micron <sup>2</sup> )	10,840	8,875
15	Dot Shape Factor	0.2915	0.5647
	Print Mottle		
	Primary Colors (CMY*)	No	No
	Secondary (RGB**)	Visible	No
	Black	Visible	No
20	Wicking	Some	Minimum
	Bleeding	Some	Minimum
	Water Fast Resistance	Good	Good
	% Coating Solids	< 25%	30-40%

25 \* "CMY" Means Cyan, Magenta, and Yellow.

\*\* "RGB" Means Red, Green and Blue.

The conclusions were as follows: Both paper samples were close in color ink density values and water fast resistance. However, the black ink density of  
 30 the sample with the inventive coating composition was 0.35 points higher than that of the commercial paper sample. The paper sample with the inventive coating composition exhibited smaller dot areas and a higher dot shape factor, indicating a better dot roundness and a lower dot gain. The percent coating solids of the commercial sample paper was also lower at less  
 35 than 25% than that of the inventive sample (30-40%), which factor most likely contributed to the print mottle problem of the commercial paper whereby the coating penetrated to the base stock.

### 3) First Coating Trial

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day, the coating rheology and coating solids were rechecked. The coating solids and the Hercules high shear viscosity were unchanged remaining at 32% solids and 57.3 cps, respectively. However, the Brookfield low shear viscosity dropped from 720 cps to 180 cps. This was probably due to the relaxing of the cationic polymer and may represent a "plus" in that the lower shear viscosity may help the coating color to flow more freely in the coating line.

#### 4) Second Pilot Coating Trial

The objective of this pilot trial was to compare the runnability and the printability of the inventive coating composition comprising the treated calcined clay and the preferred coating formulation to an ink jet coating formulation (unknown) comprising silica pigments of the prior art. The base stocks were supplied by Otis Specialty, Inc., and the operating parameters of the roll gate coater for each paper machine line were set up as close together as possible. The speed of each coater was 800 feet per minute. The target coat weights were 2, 3, 5, and 8 pounds per 3300 ft<sup>2</sup> or about 3.0, 4.5, 7.5, and 12 g/m<sup>2</sup> per side of base stock.

The coating properties, the coated sheet properties, and the printing properties for the silica pigment of the prior art and for the treated calcined clay pigment of the invention are given in Table IV. As stated herein above the coating formulation and the kinds of chemicals for the inventive clay pigment were essentially the same as that in 3) First Coating Pilot Trial described hereinabove.

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TABLE IV

5	Coating Properties:	<u>Prior Art</u>	<u>Invention</u>
	% Coating Solids	32	34
10	OBA Added	3%	0
	Brookfield Viscosity		
	Spindle #	5	5
	@ 10 rpm	3560 cps	8400 cps
	@ 20 rpm	2440 cps	5400 cps
15	@ 50 rpm	1530 cps	2800 cps
	@ 100 rpm	1180 cps	1740 cps
	Hercules Viscosity		
20	@ 4400 rpm (kilodyne-cm)	5200	3000
	Bob	E	E
	Spring (kilodyne-cm)	400	400
	pH	9.0	7.9
	Temp.	23.5°C	24°C
25	Coated Sheet Properties		
	Coat Weight (gsm)	5.3	5.41
30	Brightness (ISO)	94.96	90.16
	Fluorescence Component (%)	6.23	0.16
	Hunter		
	L	95.01	95.21
	a	0.69	-1.0
	b	-3.79	0.70
35	Printing Properties		
	Ink Density		
	Cyan	1.48	1.48
	Magenta	1.48	1.47
	Yellow	1.10	1.09
	Black	1.27	1.43
40	Print Mottle		
	Primary Colors (CMY*)	No	No
	Sec. Colors (RGB**)	No	No
	Black	No	No
45	Wicking	Minimum	Minimum
	Bleeding	Minimum	Minimum
	Water Fastness Resistance	Yes	Yes
50	* "CMY" Means Cyan, Magenta and Yellow.		
	** "RGB" Means Red, Green and Blue.		

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The pilot trial provided excellent information particularly with regard to the runnability of the coatings on a gate roll coater. When its coating speed was at 800 feet per minute, the base stock with the inventive coating performed much better than that with the silica coating of the prior art. The  
5 base stock with the silica coating of the prior art tended to form large sized splitting patterns on the applicator, resulting in a rejectable rough sheet surface. It also showed significant coating misting problems during the trial, and dusting on the coated sheets was visible. Conversely, the paper with the inventive coating composition did not experience these problems. The  
10 coating was very stable on the coater's applicator, and it was easy to produce a wider range of coat weights such as 6 lbs. to about 11 lbs. per 3300 ft<sup>2</sup> (9-16.5 g/m<sup>2</sup>) per side. The coated sheet with the inventive composition visually appeared to be much smoother than that of the prior art.

The base stock with the inventive coating showed a lower brightness  
15 value than that of the prior art. It is hypothesized that this is due to the fact that no optical brightening agents were added to the coating composition in this trial. The printing performance of these two coating colors was very similar, except for the black ink density where the black ink density for the paper with the inventive coating was higher at 1.43 compared to 1.27 for  
20 that of the prior art. This fact can be considered to be an important pigment feature where print contrast is important.

#### Competitive Product vs. Invention

A further test was performed on an ink jet paper with a silica coating commercially available from Degussa, Inc. under the tradename FK 310, and  
25 on an ink jet paper prepared with the inventive coating. Their physical properties are shown in Table V.

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TABLE V

<u>Physical Properties</u>		<u>Invention</u>	<u>Prior Art</u>
5	Brightness (ISO)	89.9	98.02
	Hunter Color		
	L	86.74	98.72
	a	-0.33	0.32
10	b	3.23	-0.06
	Residue + 100 (%)	0.0002	0.0024
	Residue + 200 (%)	0.0006	0.0008
	Residue + 325 (%)	0.0071	0.0020
15	Einhöner Abrasion (mg) @ 100,000 revolutions	12.4	6.6
	pH	4.0	3.9
20	Particle Size Distribution In Equivalent Spherical Diameter (E.S.D.) (Weight %)		
	< 10 microns	100	100
	< 8 microns	97.2	89.3
	< 2 microns	80.4	43.9
25	< 1 micron	79.0	25.3
	< 0.5 microns	28.9	20.0
	< 0.25 microns	1.6	20.9
30	Brookfield Viscosity cps @ 20 rpm, #2	380	2000+
	Solids % Slurry	31.0	32.1
35	Hercules Viscosity		
	Bob	A	A
	Dynes at	18.0	18.0
	rpm	2285	400
40			

The important point of the results shown above is that the invention has better Brookfield and Hercules high sheer viscosities compared to the prior art. The prior art composition tended not to circulate properly in the coater, and tended to form split patterns and coating misting on the waters.

From the above, it can be seen that the inventive coating composition provides a high performance, ink jet coating pigment for making a matte finish coated ink jet paper. The product specifications for this coating composition of the invention appears in Table VI below:

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TABLE VISpecification For Ink Jet Coating Pigment Of The Invention

5	Brightness Range:	88-92 ISO
	Particle Size Distribution (E.S.D. in weight %)	
	< 10 microns	100
	< 5 microns	96-98
10	< 2 microns	88-92
	< 1 micron	78-82
	< 0.6 microns	28-32
	< 0.25 microns	< 2
	% Slurry Solid	30-32
15	Brookfield Viscosity	400-800 @ 20 rpm, 32% solid
	Hercules Viscosity	18 dynes at 900-1200 rpm, A Bub
	pH	3.6 - 5.0
	Abrasion	Max. 10 mg @ 100,000 revolutions
20	Residue	Max. 0.25%

Two Recent Lab Studies

Recently, the inventors performed two lab studies to understand the influence of the type of pigment and latex binder with respect to coating on a paper and the printing properties of the coating.

First Recent Lab Study

In the first recent lab study, six different pigments were used while the coating formulation was kept constant for these six different pigments. The data is shown in Table VII.

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TABLE VII

	Inventive Pigment	ECC <sup>®</sup>	Astragaze <sup>®</sup>	Albacar	Bentonite-H	Carbilux <sup>®</sup>
5						
	Coating Properties					
	a) Solid	35	34.5	34.7	34.8	22.3
	Precipitate	No	Yes	Yes	No	No
10	Dispersion	Good	Poor	Poor	Good	Poor
	nH	6.8	7.1	6.8	7.8	7.3
	Brookfield Viscosity					
	Stompa #	5	5	5	5	5
	@10	14,300	0,720	7,840	0,380	12,400
15	@20	8,800	5,300	5,500	4,020	7,500
	@50	4,080	2,520	2,840	2,580	4,000
	@100	2,050	1,580	1,780	1,500	2,720
	Heteroex					
20	@4400 (Heteroex-est)	3,400	2,200	2,500	3,000	3,600
	Bob	E	E	E	E	E
	Printing Properties					
	Color Density					
25	Cyan	1.53	1.23	1.25	1.38	1.38
	Magenta	1.54	1.28	1.32	1.50	1.30
	Yellow	1.13	1.06	1.07	1.17	1.11
	Black	1.81	1.65	1.68	1.65	1.58
	ink Drying Rate					
30	Pst. Colors (C,M,Y)	Fast	Fast	Fast	Fast	Fast
	Sec. (R,G,B)	Fast	Slow	Slow	Fast	Slow
	Black	Fast	Slow	Slow	Fast	Slow
	Water Fastness Resist.	Good	Good	Good	Good	Fair
	Print Mottle	No	Yes	Yes	Yes	Yes
35	Wicking	Min.	Min.	Min.	Some	Min.
	Bleeding	Min.	Some	Min.	Some	Min.
	Coating Formulation:					
	Pigment 30 g					
40	Water 70 g					
	PVOM (30%): 20 cc (binder) (Aerof 103)					
	Latex CP 654MA (50%) 30 cc (binder)					
	HTI 5800m 30 cc (cross-linking agent)					

45

KCS<sup>®</sup> and Astragaze<sup>®</sup> are hydrous kaolin clays, the trademarks of which are owned by ECC International Inc., the assignee of the present invention. Albacar is a precipitated calcium carbonate, a tradename of the Pfizer Corporation. Bentonite-H is a hydrous kaolin clay supplied by Allied Colloids. Carbilux<sup>®</sup> is a ground calcium carbonate, the tradename of which is owned by the assignee of the present invention.

From the data, it is to be noted that the dispersion of the inventive pigment (calcined kaolin clay treated with cationic polymer) was "good" compared to most of the other pigments. It is to be particularly noted that the color densities for the inventive pigment improved over that of the prior art pigments, and that there was no print mottle, and a minimum amount of wicking and bleeding with the inventive pigment.

#### Second Recent Lab Study

The second recent study involved both the inventive pigment and the chemicals of the preferred coating formulation of the invention where the



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cationic polymer (Hydraid 2060) was held constant while the dosages for the polyvinyl alcohol and latex varied. The data is shown in Table VIII. From the table, it can be seen that No. 6 gives the optimum color density results at 1.47, 1.39, 1.03, and 1.47 for 14 parts Hydraid 2060, 20 parts polyvinyl alcohol, and 20 parts latex.

TABLE VIII

Sample ID	Ctrl.	1	2	3	4	5	6	7	8
10 HD (Hydraid 2060)	14	14	14	14	14	14	14	14	14
Airvol "PVOM (30%)	20	25	30	26	29	20	20	23	25
Latex CP 654MA (Latex)	0	0	0	5	10	15	20	5	10
Printing Properties									
15 Color Density									
Cyan	1.39	1.40	1.41	1.42	1.45	1.45	1.47	1.43	1.46
Magenta	1.18	1.21	1.24	1.20	1.20	1.34	1.39	1.21	1.35
Yellow	0.82	0.85	0.88	0.85	0.83	0.90	1.02	0.86	0.95
Black	1.40	1.46	1.48	1.40	1.48	1.48	1.47	1.39	1.46
20 Ink Drying Rate									
Pn, Colors (C,M,Y)	Fast	Fast	Fast	Fast	Fast	Fast	Fast	Fast	Fast
Sec. Colors (R,G,B)	Fast	Fast	Fast	Fast	Fast	Fast	Fast	Fast	Fast
Black	Fair	Fair	Fair	Fair	Fair	Fair	Fair	Fair	Fair
Water Fast. Resist.	Good	Good	Good	Good	Good	Good	Good	Good	Good
25 Paper Mottle	No	No	No	No	No	No	No	No	No
Wicking	Min.	Min.	Min.	Min.	Min.	Min.	Min.	Min.	Min.
Bleeding	Min.	Min.	Min.	Min.	Min.	Min.	Min.	Min.	Min.
Rev. Text	Good	Good	Good	Good	Good	Good	Good	Good	Good
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The results of Table VIII may be indicative of the fact that the cationic polymer, the polyvinyl alcohol binder, and the latex binder may all contribute to improve the color density for the inventive pigment. These results may substantiate the fact that the cationic polymer acts as a dispersant according to the teachings of the invention, and that it provides good water fastness at the pigment/polymer ratio of about 4 to 1.

While the present invention has been particularly set forth in terms of specific embodiments thereof, it will be understood in view of the instant disclosure that numerous variations upon the invention are now enabled to those skilled in the art, which variations yet reside within the scope of the present invention. Accordingly, the invention is to be broadly construed and limited only by the scope and spirit of the claims now appended hereto.

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WHAT IS CLAIMED IS:

1. A coating composition which comprises: a) an aqueous slurry containing about 30 to about 70 weight % solids, based on the weight of said aqueous slurry, of a calcined kaolin clay; and b) an effective amount of a cationic polymer or cationic polymer admixture, wherein said cationic polymer or cationic polymer admixture reacts with said calcined kaolin clay and wherein said effective amount is an amount of cationic polymer sufficient to produce a net positive charge on said calcined kaolin clay.
2. The coating composition of Claim 1 wherein said effective amount is about 5 to about 50 parts per 100 parts of said calcined kaolin clay, on an active weight basis.
3. The coating composition of Claim 1 wherein said cationic polymer has a molecular weight of about 1000 to about 5 million daltons.
4. The coating composition of Claim 1 wherein said cationic polymer is selected from the group consisting of polyamines, polydialkyldiallylammonium halides, and copolymers prepared using a dialkyldiallylammonium halide.
5. The coating composition of Claim 1 wherein said calcined kaolin clay in aggregate form has a mean pore size less than about 0.80 microns in diameter, and a particle size distribution such that about 90% are less than 2 microns E.S.D.
6. The coating composition of Claim 1 wherein said calcined kaolin clay has a total pore volume of about 0.60 cm<sup>3</sup>/g to about 2.00 cm<sup>3</sup>/g.
7. The coating composition of Claim 1 wherein said calcined kaolin clay, in aggregate form, has a particle size distribution being such that about 100 weight % are less than 10 microns E.S.D.; about 98 weight % are less than 5 microns E.S.D.; about 90 weight % are less than 2 microns E.S.D.; about 80% are less than 1 micron E.S.D.; about 30 weight % are less than 0.5 micron E.S.D.; and about 2 weight % are less than 0.25 micron E.S.D.

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8. The coating composition of Claim 1 wherein said aqueous slurry further comprises:

about 20 to about 30 parts by weight, on an active basis, per 100 parts by weight said calcined kaolin clay, of a polyvinyl alcohol binder;

about 30 to about 50 parts by weight, on an active basis, per 100 parts by weight said calcined kaolin clay, of a latex binder; and

about 0 to about 5.0 parts by weight, on an active basis, per 100 parts by weight said calcined kaolin clay, of a cross-linking agent.

9. The coating composition of Claim 8 wherein the ratio of said calcined kaolin clay to said polyvinyl alcohol binder to said latex binder on a dry weight basis ranges from about 1.0:0.15:0.05 to about 1:1:1.6.

10. A composition comprising: a) a coating substrate; and b) an effective amount for the purpose of coating said substrate of the coating composition of Claim 1.

11. The composition of Claim 10, wherein said coating substrate is a substrate useful in ink jet printing.

12. A method of preparing a coating composition for coating a substrate, comprising: a) preparing a calcined kaolin clay aqueous slurry containing about 30 to about 70 weight % solids, based on the total weight of said aqueous slurry; and b) adding an effective amount of at least one cationic polymer to said aqueous slurry, thereby dispersing said clay and producing a net positive charge on said clay.

13. The method of Claim 11, further comprising the steps of: adding about 20 to about 30 parts by weight, on an active basis, per 100 parts by weight of said calcined kaolin clay, of a polyvinyl alcohol binder; about 30 to about 50 parts by weight, on an active basis, per 100 parts by weight of said calcined kaolin clay, of a latex binder; and about 0 to about 5.0 parts by weight, on an active basis, per 100 parts by weight of said calcined kaolin clay, of a cross-linking agent.

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14. The method of Claim 12 wherein the ratio of clay to polyvinyl alcohol binder to latex binder on a dry basis ranges from about 1.0:0.15:0.05 to about 1.0:1.0:1.6.

15. The method of Claim 11, further comprising drying the product produced by the method of Claim 11 to produce a moisture-free calcined clay pigment coated with the cationic polymer.

16. The method of Claim 11, further comprising filtering the product produced by the product of Claim 11 through at least a 50 mesh sieve to remove undispersed particles and agglomerates.

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